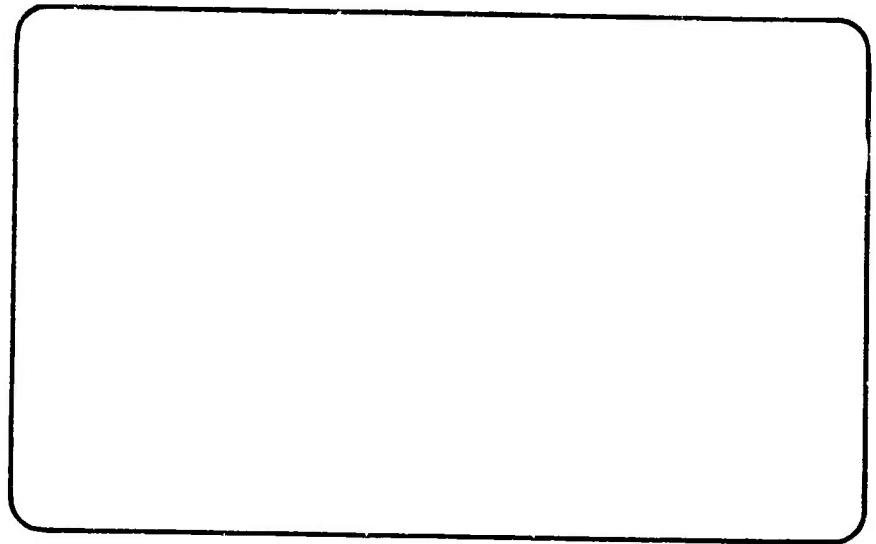




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Metal Corrosion in
Deep-Ocean Environments

Assignment 86 116
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ABSTRACT

Experiments were conducted in deep-ocean environments to determine whether unusual corrosion phenomena exist at great depths that are not present in water near the surface. A total of five exposures were made at various locations in the Pacific Ocean. Two exposures were at 5640 feet, and one each at 2340, 5300, and 6780 feet. In some cases, similar tests were conducted in shallow water. Results from general corrosion tests of metals representing six typical alloy classes, and also from crevice-corrosion tests on a stainless steel and nickel alloy, revealed that, in general, there were no major differences between corrosion phenomena in deep-ocean and shallow-water environments. Variations in behavioral patterns that were observed could largely be explained on the basis of differences in oxygen content.

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ADMINISTRATIVE INFORMATION

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INTRODUCTION

This investigation was undertaken to determine whether unusual corrosion phenomena exist at great ocean depths that are not present in water near the surface. Knowledge of the corrosion behavior of metals in the deep ocean is of interest to the U. S. Navy because of the need for constructional materials in the conquest of hydrospace.

In this article the deep ocean is defined as a depth of about 200 ft or more. Some of the most significant features of deep marine environments which differ greatly from shallow water are low water temperature, variation of oxygen content with depth, and high hydrostatic pressure. These and other environmental factors have been described and discussed in more detail elsewhere.^{1,2}

Studies of metal corrosion in deep-ocean environments were approached from two aspects: (1) a corrosion survey of materials representing various important alloy classes, and (2) an investigation of crevice corrosion in selected passive metals.

The general corrosion tests were designed to study the total effect of all environmental parameters on the behavior of typical classes of alloys susceptible to various forms of attack in surface water.

Changes in oxygen content with depth and crevice size were the main variables examined in the crevice-corrosion tests. Crevice corrosion (and pitting) in passive metals is initiated when anodic areas form by the combined action of differential oxygen concentration cells and the chloride ion. This situation is established when one area of the metal is freely exposed to the environment and the other shielded. Localized attack then proceeds by galvanic action between active (oxygen deficient) and passive areas on the metal surface. Other investigators have shown³ that the extent of attack is a function of the size relationship between the active and passive surfaces. The degree of attack decreases with increasing crevice area, and vice versa. Since crevice corrosion in passive metals is mainly an oxygen-dependent process, it was postulated that the phenomenon could be better characterized by studying the additional effect produced by varying the crevice size.

MATERIALS

Metals representing six alloy classes were employed in the material survey. Type 304 stainless steel and Monel 400 (nickel

alloy) were the two metals used in the crevice-corrosion studies. The alloy types are listed in Table 1 together with their designations and nominal compositions.

THE INVESTIGATION

Exposures in deep-ocean environments were made in the Pacific Ocean in cooperation with, and on submersible test units of, the U. S. Naval Civil Engineering Laboratory, Port Hueneme, California. In some cases, similar experiments were also conducted in shallow water at the Harbor Island Corrosion Laboratory, Wrightsville Beach, North Carolina. In the general corrosion studies, materials were tested at depths of 5640 ft for 123 days and 751 days, 5300 ft for 1064 days, and in water just below the surface for 386 days. Crevice-corrosion experiments were made at depths of 2340 ft for 197 days, 6780 ft for 403 days, and in shallow water for 238 days. The test materials were not buried in nor covered by the bottom sediments in the deep-ocean exposures, although the submersible test units were placed on the ocean floor. Water chemistry, temperature, and other environmental conditions were measured and observed at both locations.

Corrosion of the materials was evaluated in terms of weight loss, pit depth, corrosion rate, and appearance. In some cases microscopic examinations were conducted. In addition, cross sections of some of the copper-base alloys were fractured and examined

macroscopically and microscopically for evidence of selective-phase corrosion.

General Corrosion Experiments

Rectangular metal panels (12 in. x 2 in.) were used in the three deep-marine exposures. The samples were from 1/16 to 1/4 in. thick. A hole was drilled at each end for attachment to a rack, and plastic sleeves and washers were used to avoid galvanic coupling between metallic components. The dimensions of specimens in the shallow-water immersion were 12 in. x 3 in. x 1/16 in. A hole was drilled in the center for mounting purposes, and again the samples were isolated electrically with plastic parts. In all of these tests, a crevice of constant area existed on each specimen due to the contact area created by the nonmetallic supporting fixtures.

Twenty-three specimens were exposed in each experiment at 5640 ft, ten at 5300 ft and ten in shallow water. A zinc anode was attached to a sample of 1015 steel in each deep-ocean exposure to test effectiveness in providing cathodic protection to a more noble material at these depths.

Crevice-Corrosion Experiments

Specimens of the 304 stainless steel were 12 in. x 2 in. x 1/8 in., and those of the Monel 400 were 12 in. x 2 in. x 1/16 in. The test arrangement is shown in Figure 1. Each side of the rack

contained eight samples of identical material. The crevice area was varied from 0 to 14 sq. in. on both faces of the specimens by means of the tree-shaped nylon strips. Also used to electrically insulate the samples from the steel rack were nylon strips, with a constant area, thereby introducing an additional 8 sq. in. crevice on each face of the alloys. A zinc-base paint and zinc anode were employed for corrosion protection of the rack.

RESULTS AND DISCUSSION

Average environmental characteristics for six parameters in the studies appear in Table 2. The most pronounced variations at the different depths were the oxygen content, temperature, and pressure. Fouling by marine organisms was quite heavy on many of the metal panels and racks in the surface water, but was negligible in the deep-ocean exposures.

Results of the general corrosion experiments are summarized in Table 3, and examples of tested specimens are shown in Figures 2 and 3. Data from the crevice-corrosion studies are presented in Figures 4 and 5. Pit depths, used as a measure of crevice attack in the general and crevice-corrosion experiments, represent the maximum attack inside the crevice areas, or at the entrance to the crevices formed by contact of the metallic specimens and the insulators or nylon strips.

General Corrosion Experiments

The results of these experiments are discussed below in terms of alloy types.

Carbon Steel. AISI 1015 steel (no zinc anode attached) was more uniformly corroded in the deep-ocean exposures than in shallow water. Corrosion was also more extensive in water just below the surface. Comparison of the corrosion behavior of the alloy in shallow water (Exposure 4) and in the deep ocean (Exposure 3) appears in Items (a) and (b) Figure 2. Large depressions are observed on the specimen tested in surface water, while the alloy in the deep ocean was more evenly attacked. Zinc anodes were effective in reducing the corrosion of the steel specimens. Considerable differences in overall corrosion and crevice attack can be shown by comparing the data for samples with and without the anode in Table 3.

Stainless Steels. Severe crevice attack of these alloys occurred in all exposures. In addition, 304 stainless steel suffered pitting on the boldly exposed surface in all of the tests with the exception of Exposure 1 (5640 ft, 123 days). The freely exposed surface of AM 350 was unblemished in all experiments.

Copper Alloys. Minor attack occurred on copper and the cupro-nickel alloys (10 and 30 percent) in both surface and deep-ocean experiments. More pronounced attack was present on copper

in shallow water than in deep water as shown in Items (c) and (d), Figure 2. Microscopic and macroscopic examinations of the remaining copper alloys revealed selective-phase corrosion only in the case of high-tensile brass. This attack (dezincification) extended about 0.06 in. below the surface on each side of the specimen in the test conducted for 751 days at 5640 ft (Exposure 2). Attack was considerably less in the short-time experiment (Exposure 1). No selective-phase attack (dealuminization) was found on the aluminum-bronze alloy specimens, all of which were in the heat-treated condition.

Nickel Alloys. Of the nickel-base alloys, Hastelloy C had superior corrosion resistance in all experiments, although changes in test conditions affected the corrosion of this material. The corrosion rate was 0.560 milligrams per square decimeter per day (mdd) in Exposure 1 (5640 ft, 123 days) as compared to 0.022 mdd in Exposure 2 (5640 ft, 751 days). This was approximately an order of magnitude decrease in the corrosion rate and was probably caused by the increase in oxygen content from 1.19 to 2.14 ppm. The higher level of oxygen would function to maintain a superior passive film.

Titanium Alloys. Differences in corrosion rate were observed for these alloys in Exposures 1 and 2. Titanium (unalloyed) and alpha-beta titanium (6Al-4V) showed a decrease of more than two

magnitudes in corrosion rate in Exposure 2 (5640 ft, 751 days), while the beta alloy (13V-11Cr-3Al) decreased by more than one magnitude. These changes can also probably be attributed to the effect of variation in oxygen on the film integrity. However, even the highest corrosion rates were of minor significance, and no evidence of attack on any specimen was apparent in visual examination.

Aluminum Alloys. Figure 3 is a photograph of the aluminum alloys tested in Exposure 2 (5640 ft, 751 days). Severe surface and crevice corrosion can be observed on all specimens. Aluminum 6061-T6 had numerous perforations (0.063 in.). The intensity of corrosion of these alloys was much greater than expected in the deep-ocean environments, especially 5456-H321 which normally has shown good resistance in surface water. Microscopic examinations showed that 7079-T6 specimens suffered severe intergranular corrosion in both exposures. A specimen of 6061-T6 was tested in Exposure 3 (5300 ft, 1064 days), but it was missing at the conclusion of the experiment. It probably was lost because of severe localized corrosion in the area of the supporting fixtures. Accelerated corrosion of the aluminum alloys in the deep ocean may be a function of the oxygen content. The low levels of oxygen could be insufficient for the formation and maintenance of necessary protective surface oxide scales. Oxygen deficiencies in some of these

deep marine environments could be detrimental to the corrosion resistance of such materials, whereas a metal like titanium would be virtually unaffected.

Crevise-Corrosion Experiments

Moderate crevice corrosion occurred on 304 stainless steel at a depth of 2340 ft (Exposure 5), but no attack was observed on Monel 400 (Figures 4 and 5). Neither material suffered any localized attack on the boldly exposed surfaces. Patches of rust were visible on the surfaces of 304 stainless steel, and various shades of green corrosion products were present on Monel 400.

In 6780 ft of water (Exposure 6), more severe deterioration took place as indicated by the increased weight losses in the case of both alloys. Incipient crevice corrosion was evident on Monel 400, especially at the nylon insulating strips, but no measurable pits were present. The increase in corrosion of the samples at this depth was probably due to an increase in oxygen content from 0.70 to 1.60 ppm as well as the longer exposure time.

Severe crevice corrosion and overall surface corrosion were quite pronounced in the shallow water investigation (Exposure 7), although one of the deep-ocean exposures (Exposure 6) was conducted for 165 days longer. These differences in behavior are reflected in the plots in Figures 4 and 5 and in the photographs of typical samples in Figure 6. Several of the stainless specimens were

perforated at the crevices and on the surfaces remote from the crevices. One of the nickel samples was perforated at the crevice.

Variations in oxygen content in the crevice-corrosion experiments appeared to be the most important factor in the behavior of 304 stainless steel and Monel 400. Oxygen concentration was 6.77 ppm in surface water as compared to 1.70 ppm and 0.60 ppm in the deep water. Lower oxygen contents in the deep-marine environments tended to minimize the effect of differential oxygen concentration cells. A great deal of the pitting in the shallow water was caused by crevices formed by fouling of the freely exposed metal surfaces. Differences in temperature also could have influenced the corrosion process.

The degree of crevice corrosion as a function of area was shown fairly well by the weight-loss measurements and visual observations for both alloys in some instances. Depth of pitting did not follow a predictable pattern on the stainless alloy in Exposures 5 and 7, but the nickel alloy did show some consistency in behavior in shallow water (Exposure 7). No measurable pits were observed on the Monel 400 specimens tested in the deep ocean. Maximum pit depth as a function of crevice size was not shown as clearly as anticipated, probably because of uncertainty in crevice geometry due to deformation of nylon components when compressed, and localized attack outside the crevice.

CONCLUSIONS

The purpose of this investigation was to determine if unusual corrosion phenomena exist at great ocean depths that are not present in water near the surface. Results from exposures of materials representing six typical alloy classes, and crevice-corrosion experiments on a stainless steel and a nickel alloy, revealed that, in general, there were no major differences between the corrosion phenomena in deep and shallow waters. Variations in the corrosion behavior that were observed could be explained for the most part on the basis of differences in oxygen content. A possible exception to this generalization is corrosion processes in the bottom sediments on the sea floor.

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Table 1
Description of Material

Alloy Type	Alloy Designation	Major Alloy Content, % ¹
Carbon Steel	AISI 1015	
Stainless Steel	AISI Type 304 AM 350	19Cr-10Ni 17Cr-4Ni-3Mo
Copper	Copper (Unalloyed) Cupro-Nickel, 10% Cupro-Nickel, 30% Red Brass Naval Brass High Tensile Brass Al Bronze Al Bronze Al-Ni Bronze	10Ni-1.3Fe 30Ni-0.6Fe 15Zn 39Zn-0.8Sn 21Zn-5Al-4Mn-2Fe 10Al-3.5Fe 10Al-4Fe-2.5Ni 10Al-4Fe-4Ni
Nickel	Monel 400 ⁽²⁾ Monel K-500 ⁽²⁾ Ni-o-nel 825 ⁽²⁾ Hastelloy C ⁽³⁾	30 Cu 29Cu-3Al 30Fe-22Cr-3Mo-2Cu-1Ti 17Mo-15Cr-5Fe-4W
Titanium	Titanium (Unalloyed) Beta Alpha-Beta	13V-11Cr-3Al 6Al-4V
Aluminum	6061-T6 7079-T6 5456-H321	1Mg-0.6Si-0.25Cu-0.25Cr 4.3Zn-3.3Mg-0.6Cu-0.2Mn-0.2Cr 5Mg-0.7Mn-0.15Cu-0.15Cr

¹ Nominal percentages.

² Trademark of The International Nickel Company, Inc.

³ Trademark of Haynes-Stellite Company, Division of Union Carbide Corporation.

Table 3
Results of General Corrosion Experiments

Alloy Designation	Exposure 1	Exposure 2	Exposure 3	Exposure 4	Surface Attack (Outside Crevice Area)	Crevice Attack (Maximum Pit Depth)
	5640 Feet, 123 Days Corrosion Rate mdd(1),(2)	5640 Feet, 751 Days Corrosion Rate mdd(1),(2)	5300 Feet, 1064 Days Corrosion Rate mdd(1),(2)	Surface, 386 Days Corrosion Rate mdd(1),(2)		
<u>Carbon Steel</u>						
AISI 1015(3)	16.5	9.52	3.16	28.7	Uniform corrosion in Exposures 1, 2, and 3. Overall irregular corrosion in Exposure 4.	At crevice entrance as follows: Exposure 1 = 0.007 in., Exposure 2 = 0.010 in., Exposure 3 = 0.020 in., Exposure 4 = 0.015 in.
AISI 1015(4)	1.42	4.60(5)	2.17(5)	-	Uniform corrosion in Exposures 1, and 2. Uniform to irregular corrosion in Exposure 3.	At crevice entrance as follows: Exposure 1 = 0, Exposure 2 = 0.003 in., and Exposure 3 = 0.005 in.
<u>Stainless Steels</u>						
AISI Type 304	5.91(6)	8.51(6)	5.31(6)	3.15(6)	No visible pits in Exposure 1. Severe pitting and edge attack at scattered areas in Exposure 2 and 3. Attack along all edges + perforations (0.063 in.) at scattered points in Exposure 4.	Inside crevice as follows: Exposure 1 = 0.031 in., Exposures 2, 3 = 0.125 in. (perforated), Exposure 4 = 0.063 in. (perforated).
AM 350	1.43(6)	6.29(6)	2.83(6)	-	No visible corrosion in Exposures 1, 2, and 3.	Inside crevice as follows: Exposure 1 = 0.043 in., Exposures 2, 3 = 0.063 in. (perforated).
<u>Copper Alloys</u>						
Copper (unalloyed)	12.1	3.78	2.65	4.50(6)	Slight surface etching in Exposures 1, 2, and 3. Etching + moderate edge attack in Exposure 4.	No attack in Exposures 1 and 2. At crevice entrance as follows: Exposure 3 = 0.001 in., Exposure 4 = 0.005 in.
Cupro-Nickel 10%	5.66	3.23	3.54	1.66	Slight to moderate surface etching in Exposures 1, 2, and 4. Etched + streaked in Exposure 3.	No attack in Exposures 1 and 2. Slight attack at crevice entrance in Exposures 3 and 4.
Cupro-Nickel 30%	6.27	2.75	3.08	1.42	Etched in Exposures 1 and 4. Etched + streaked in Exposures 2 and 3.	No attack in Exposure 1. Slight attack at crevice entrance in Exposures 2, 3, and 4.
Red Brass	11.5	4.04	3.99	5.05	Etched in all exposures.	No pitting in any exposures.
Naval Brass	7.04	3.33	3.85	3.89	Etched in all exposures.	No pitting in any exposures.
High Tensile Brass	8.50	17.3	-	-	Surface discoloration indicative of dezincification in both exposures.	No pitting in any exposures.

(1) For explanation of footnotes, see third portion of this table.

Table 3 (cont.)

Alloy Designation	Exposure 1	Exposure 2	Exposure 3	Exposure 4	Surface Attack (Outside Crevice Area)	Crevice Attack (Maximum Pit Depth)
	5640 Feet, 123 Days	5640 Feet, 751 Days	5300 Feet, 1064 Days	Surface, 386 Days		
	Corrosion Rate mdd(1), (2)	Corrosion Rate mdd(1), (2)	Corrosion Rate mdd(1), (2)	Corrosion Rate mdd(1), (2)		
<u>Copper Alloys (cont.)</u>						
Al Bronze(7)	2.27	1.43(6)	-	-	No visible attack in Exposure 1. General pitting to 0.002 in. Exposure 2.	No attack in Exposure 1. Attack at crevice entrance to 0.011 in. in Exposure 2.
Al Bronze(8)	3.10(6)	2.02(6)	-	-	Random pitting on one side of specimen to 0.002 in. in Exposure 1. General pitting to 0.021 in. in Exposure 2.	Attack at crevice entrance as follows: Exposure 1 = 0.001 in., Exposure 2 = 0.021 in.
Al-Ni Bronze	2.65	1.08(6)	-	-	No visible attack in Exposure 1. General pitting to 0.001 in. in Exposure 2.	No attack in Exposure 1. At crevice entrance to 0.021 in. in Exposure 2.
<u>Nickel Alloys</u>						
Monel V	3.06	0.738(6)	-	8.03(6)	Etched, tarnished, and streaked in Exposures 1 and 2. Severe surface pitting to 0.020 in. in Exposure 4.	Inside crevice and at crevice entrance as follows: Exposure 1 = incipient, Exposure 2 = 0.013 in., Exposure 4 = 0.063 in. (perforated).
Monel K-500	4.37(6)	2.26(6)	-	7.97(6)	Etched in Exposure 1. General surface pitting to 0.008 in. in Exposure 2 and 0.033 in. in Exposure 4.	Inside crevice and at crevice entrance as follows: Exposure 1 = 0.011 in., Exposure 2 and 4 = 0.053 in. (perforated).
Ni-0-nel 825	0.634	2.31(6)	-	0.218(6)	No visible attack in Exposure 1. Scattered pitting to 0.001 in. in Exposure 2 and 0.002 in. in Exposure 4.	Inside crevice as follows: Exposure 1 = incipient, Exposure 2 = 0.053 in. (perforated), and Exposure 4 = 0.057 in.
Hastelloy C	0.560	0.022	-	-	No visible attack in any exposures.	None.
<u>Titanium Alloys</u>						
Titanium (unallloyed)	0.601	0.005	-	-	No visible attack in any exposures.	None.
Beta	0.004	0.002	-	-	No visible attack in any exposures.	None.
Alpha-Beta	0.569	0.001	-	-	No visible attack in any exposures.	None.

Table 3 (cont.)

Alloy Designation	Exposure 1	Exposure 2	Exposure 3	Exposure 4	Surface Attack (Outside Crevice Area)	Crevice Attack (Maximum Pit Depth)
	5640 Feet, 123 Days Corrosion Rate mdd(1),(2)	5640 Feet, 751 Days Corrosion Rate mdd(1),(2)	5300 Feet, 1064 Days Corrosion Rate mdd(1),(2)	Surface, 386 Days Corrosion Rate mdd(1),(2)		
<u>Aluminum Alloys</u>						
6061-T6	6.94(6)	4.96(6)	-(9)	-	Numerous scattered pits to 0.027 in. in Exposure 1. Severe edge attack + perforations (0.063 in.) in Exposure 2.	At crevice entrance to 0.021 in. in Exposure 1. Specimen perforated (0.063 in.) at crevice entrance and inside crevice in Exposure 2.
7079-T6	1.24(6)	4.15(6)	-	-	Scattered pitting to 0.004 in. in Exposure 1. One side pitted to 0.041 in. in Exposure 2.	At crevice entrance to 0.009 in. in Exposure 1. Inside crevice to 0.080 in. in Exposure 2.
5456-H321	2.39(6)	4.14(6)	-	-	Scattered pitting to 0.005 in. in Exposure 1. Extensive edge attack + pitting to 0.017 in. in Exposure 2.	Inside crevice to 0.005 in. in Exposure 1 and 0.023 in. in Exposure 2.

¹mdd = milligrams per square decimeter per day.

²For cases where the corrosion is largely general rather than localized, the corrosion rate in inches penetration per year (ipy) can be calculated using this formula:

$$\frac{\text{density(grams/cm}^3\text{)}}{\text{mdd}} \times 0.00144$$

³Plain, no zinc anode attached.

⁴Zinc anode attached.

⁵Zinc anode missing at completion of exposure.

⁶Weight loss attributed largely to localized corrosion.

⁷Major Alloy Content: 10Al-3.5Fe.

⁸Major Alloy Content: 10Al-4Fe-2.5Ni.

⁹Specimen missing at completion of exposure.

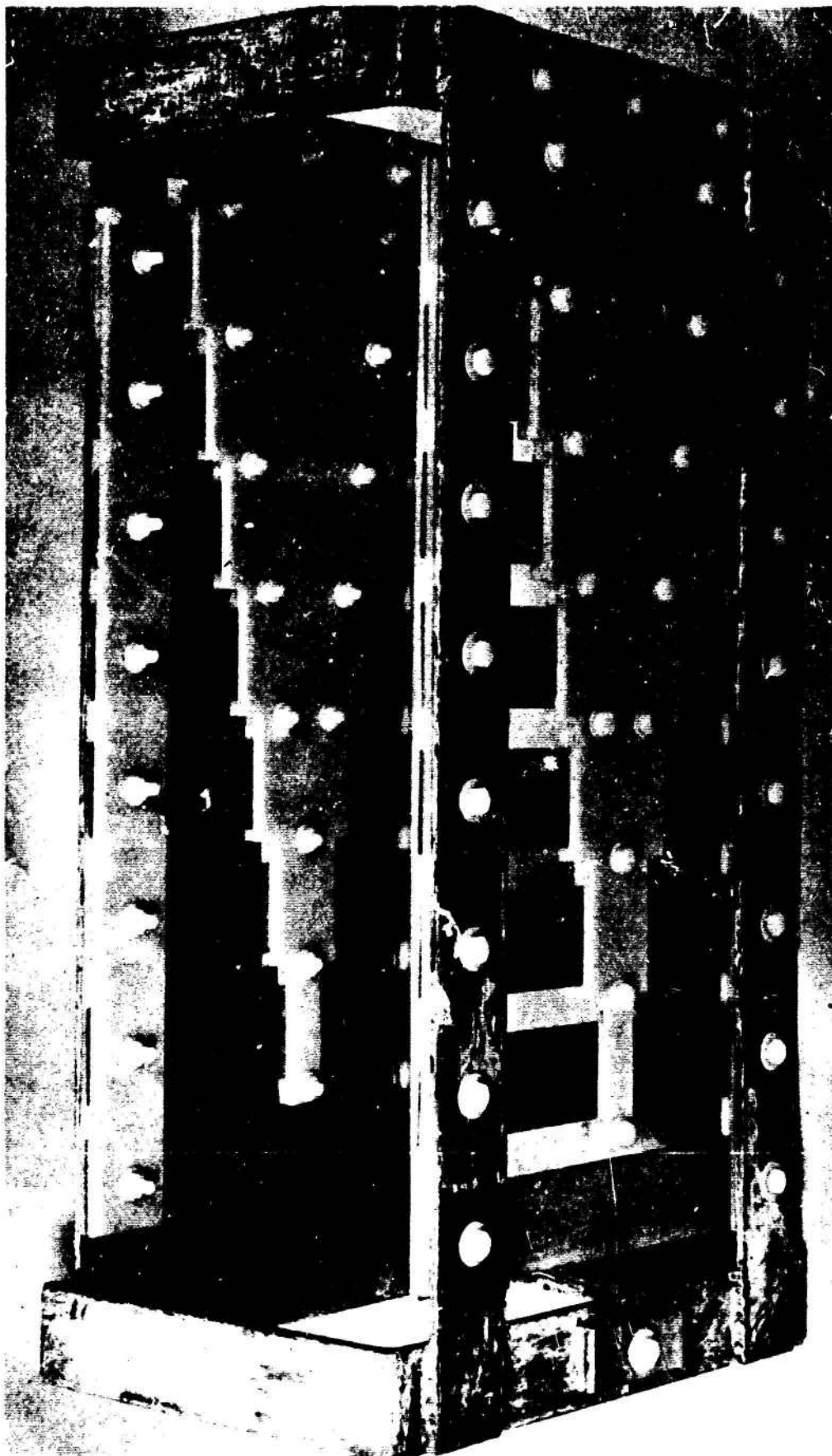


Figure 1
Rack of Crevice-Corrosion Specimens Illustrating Method of
Varying Crevice Area With Nylon Strips

- (1) 1015 Steel, Surface - 386 Days (Exposure 4)
- (2) 1015 Steel, 5300 Ft - 1064 Days (Exposure 3)
- (3) Copper, Surface - 386 Days (Exposure 4)
- (4) Copper, 5300 Ft - 1064 Days (Exposure 3)

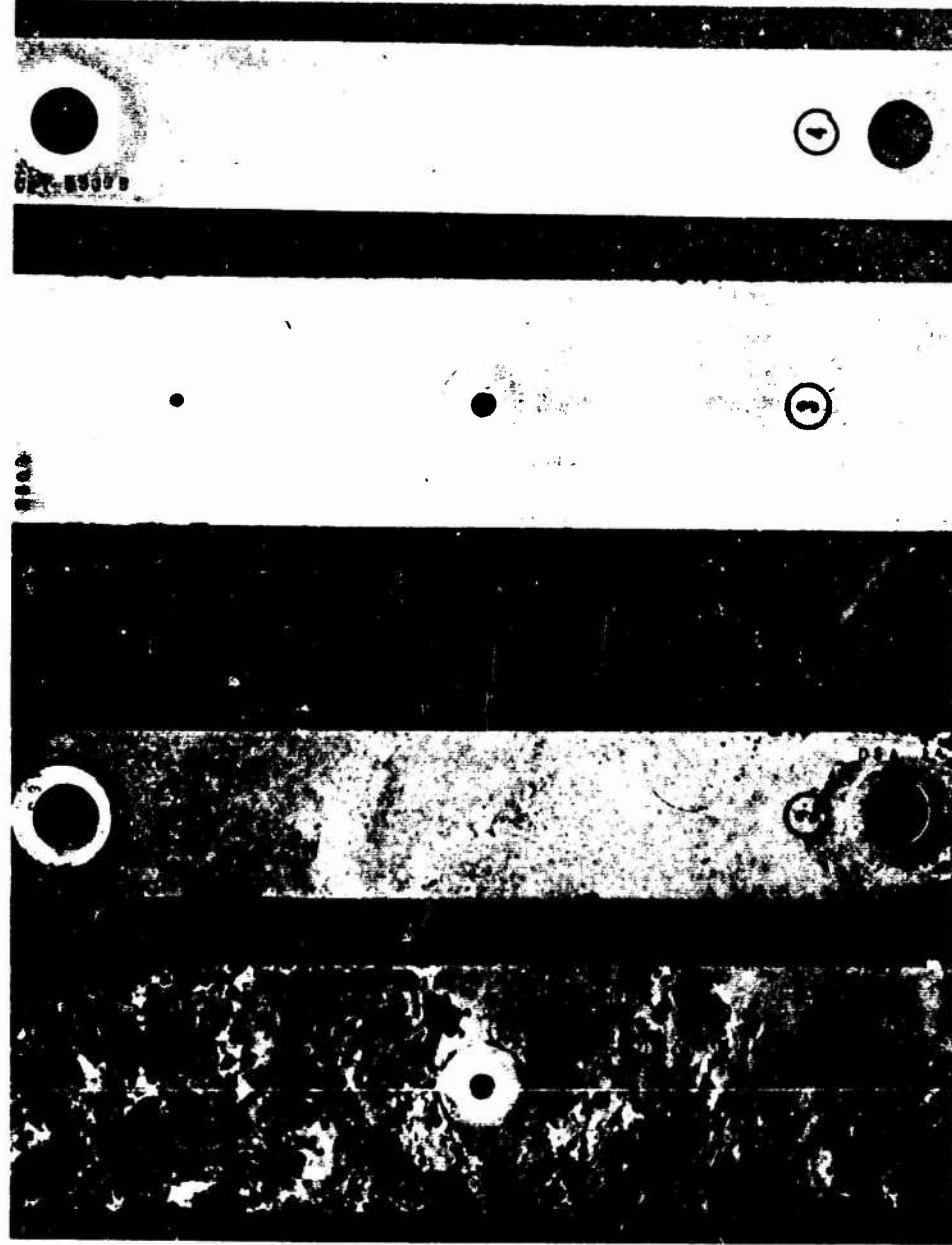


Figure 2
Comparison of Corrosion of Materials in the Deep Ocean and in Surface Water

(1) 6061-T6 (2) 7079-T6 (3) 5456-H321

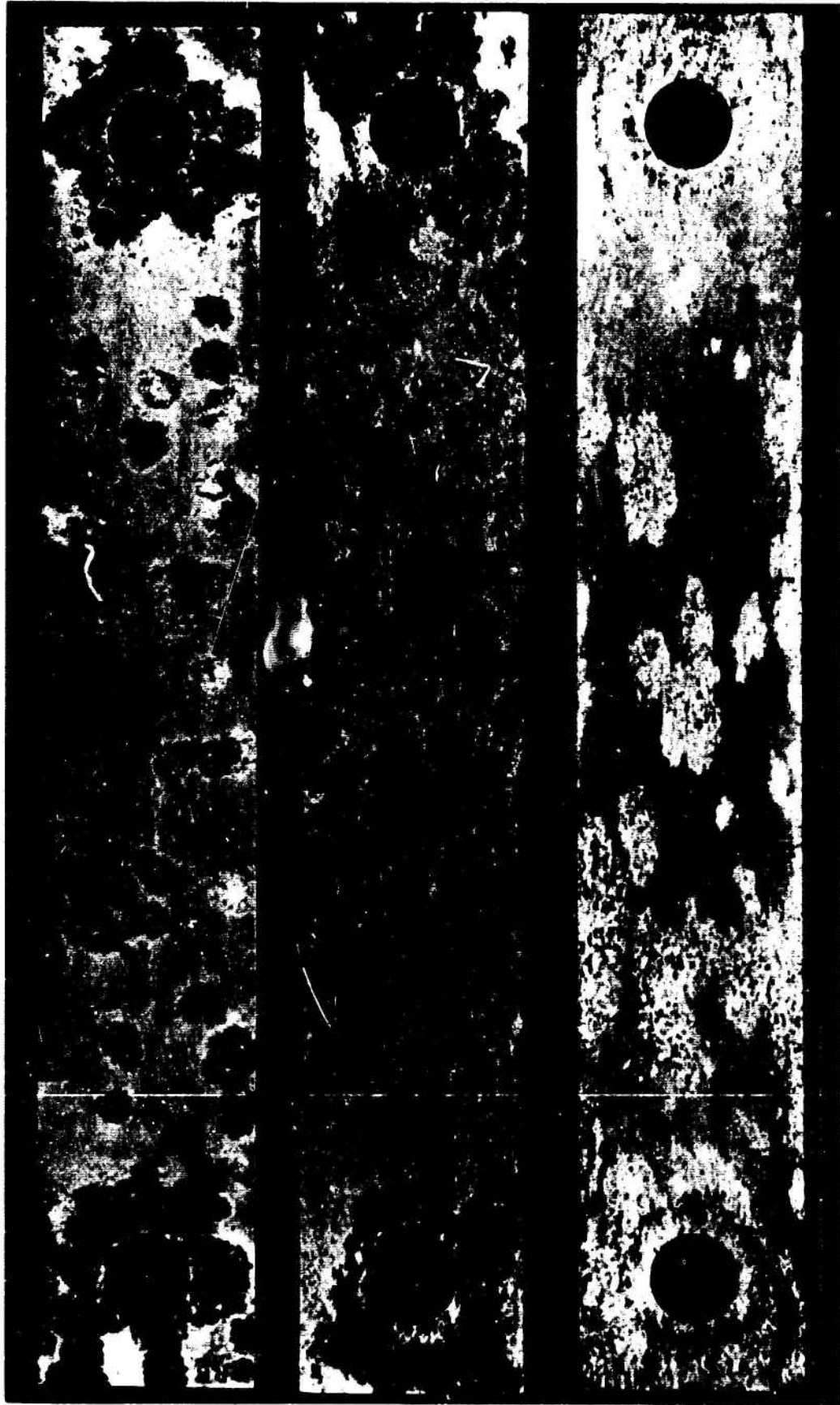


Figure 3
Appearance of Aluminum Alloys After 751 Days in 5640 Feet of Water (Exposure 2)

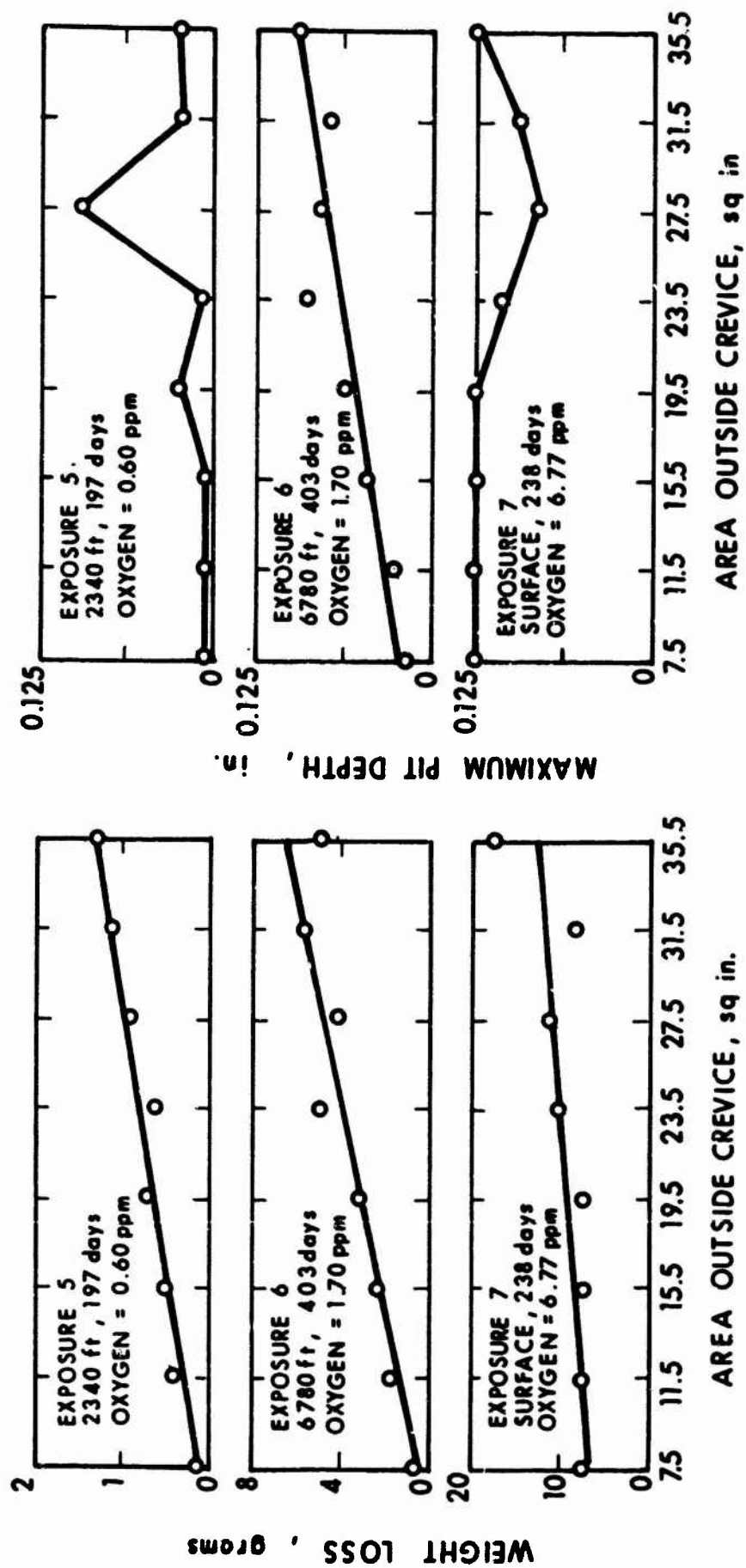


Figure 4
 Relation of Weight Loss and Maximum Pit Depth in the Crevice to Area of Specimen Outside the Crevice for Type 304 Stainless Steel at Various Depths.
 (Note: Specimen perforated at maximum pit depth = 0.125 in.)

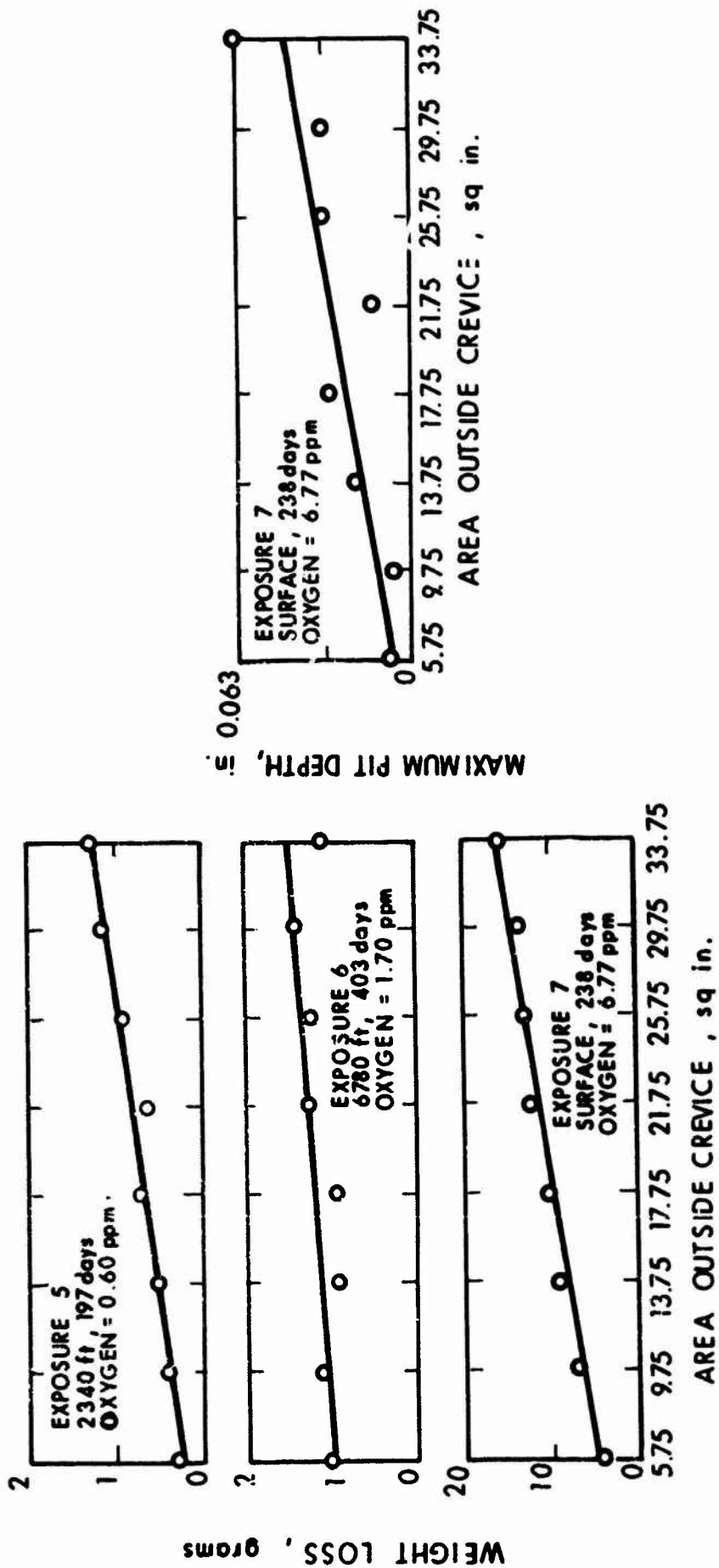


Figure 5
Relation of Weight Loss and Maximum Pit Depth in the Crevice to Area of Specimen Outside the Crevice for Monel 400 at Various Depths.
(Note: Specimen perforated at maximum pit depth = 0.063 in.)

- (1) Type 304 stainless steel, 6780 feet - 403 days (Exposure 6)
- (2) Type 304 stainless steel, surface - 238 days (Exposure 7)
- (3) Monel 400, 6780 feet - 403 days (Exposure 6)
- (4) Monel 400, surface - 238 days (Exposure 7)

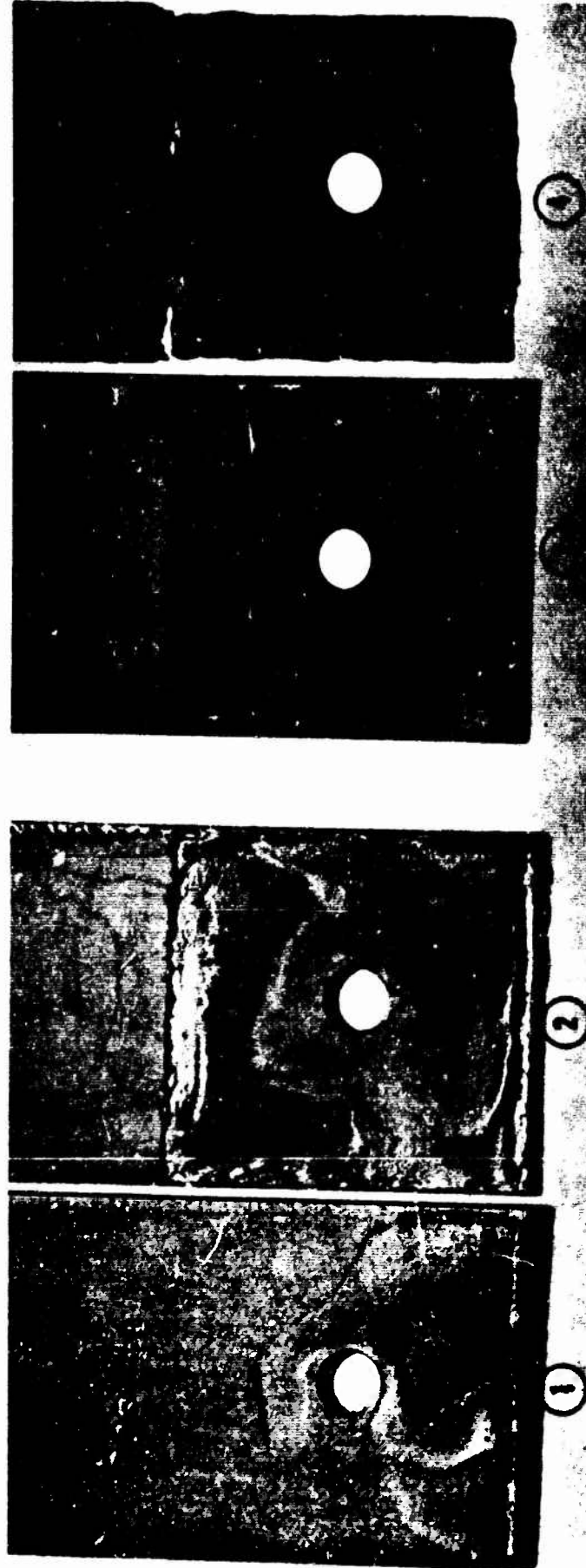


Figure 6
Comparison of Crevice Corrosion Characteristics of Materials
in the Deep Ocean and in Surface Water

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Deep Ocean Environments						
Shallow Water						
Metal Corrosion						
General Corrosion						
Crevice Corrosion						
Carbon Steel						
Stainless Alloys						
Copper Alloys						
Nickel Alloys						
Titanium Alloys						
Aluminum Alloys						